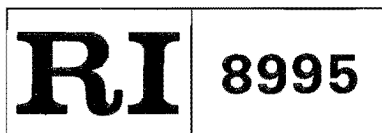


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Recovery of Metal Values From Copper Converter Flue Dust

By F. J. Palumbo, R. L. Marsh, and R. C. Gabler, Jr.



UNITED STATES DEPARTMENT OF THE INTERIOR



Report of Investigations 8995

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg/L	milligram per liter
g	gram	mL	milliliter
g/L	gram per liter	min	minute
in	inch	pct	percent
kg	kilogram	st	short ton
L	liter	st/d	short ton per day
lb/ft ³	pound per cubic foot	wt pct	weight percent
μm	micrometer		

RECOVERY OF METAL VALUES FROM COPPER CONVERTER FLUE DUST

By F. J. Palumbo,¹ R. L. Marsh,² and R. C. Gabler, Jr.¹

ABSTRACT

Effective recycling or disposal of flue dusts is a continuing problem for copper, brass, and bronze smelters. Over 300,000 short tons (st) of dust is generated annually by U.S. secondary copper, brass, and bronze smelters. The Bureau of Mines has developed an alkaline leach method for recovering metal values from copper converter flue dust containing zinc, tin, lead, and copper. The dust was leached with a hot solution of ammonium chloride and ammonium hydroxide to solubilize ZnO. All of the tin (as SnO₂) and the metallic copper, lead, and zinc, as well as possible insoluble compounds of each, report to the residue. Dissolved copper and lead salts are removed from the leachate by cementation with granular zinc. Zinc oxide is precipitated by diluting the leachate with water. The tin-rich (9.8 pct) residue has a ready market. The cement product is recyclable to the smelting operation. The ZnO is at least 97 pct pure and has potential marketability.

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INTRODUCTION

As uses for copper have increased, so has scrap utilization by secondary smelters, with resultant increases in smelter flue dust generation and problems associated with its utilization or disposal. In converting "black" copper produced from low-grade scrap, up to 0.3 st of flue dust is generated for each short ton of copper produced (1).³ In the United States, it is estimated (2) that over 300,000 st of secondary copper smelter flue dust are produced annually. A significant amount of this flue dust is produced by relatively small brass and bronze ingot makers.

Sales of flue dust for zinc content have been curtailed because of high concentrations of lead from solders as well as chlorine, probably from metals coated with polyvinyl chloride. A small amount of these zinc-bearing flue dusts is being sold to the agricultural industry as a micronutrient soil additive in commercial fertilizer. Flue dusts containing 8 pct or more tin presently can be marketed and processed to recover tin. The minimum tin content for a salable product is generally based on both world market prices for tin and transportation costs (3).

Smelter flue dust has been the subject of numerous investigations (4-7) regarding economics, disposal, and metals recovery. Metals recovery technologies studied include acidic (4) and caustic leaching (6), pyrometallurgical treatment (5), and a combination of hydrometallurgical and electrochemical processing (6-7).

Brass and bronze ingot makers have briquetted limited quantities of flue

dust containing high tin and lead values for in-house recycling. The main limitation is that much of the recycled dust reenters the gas stream without melting. This results in the production of even more dust. Mackey and Bergsoe (8) appear to have overcome this problem by melting and solidifying the dust in a special furnace. When the solidified dust is added to the charge, little of the recycled dust enters the gas stream to change the flue dust composition.

However, none of these processes (4-8) has apparently achieved industry acceptance, according to a literature review and inquiries by Bureau of Mines personnel. Economics (2, 9) or electrolyte contamination problems (4, 9-10) were cited as prohibiting factors. In its study of metallurgical recycling processes, EIC Corp. (9) nevertheless recommended further study of ZnO recovery from flue dusts using concentrated NH_4Cl solutions.

As part of its program to conserve natural resources, the Bureau initiated a study to explore alternative methods of metal recovery from flue dust. The objective was to develop an alkaline process that emphasized environmental concerns. The approach involved using a NH_4Cl - NH_4OH leach solution to solubilize ZnO. This produces a concentration of metals in the leach residue and cementation products. These metals are potentially salable or recyclable to secondary copper, brass, and bronze smelters. Zinc oxide is recovered at the end of the process as a byproduct.

PROCEDURE DEVELOPMENT

A flow sheet for the process is shown in figure 1. The process consists of a hot NH_4Cl - NH_4OH leach of copper converter flue dust. After filtering the leach residue, the dissolved copper and lead

salts are removed from the pregnant leach liquor by cementation with granular zinc metal. The cement product is filtered, and the ZnO is precipitated by diluting the filtrate with water.

For this process it was necessary to optimize the parameters to achieve maximum dissolution of ZnO during the leach, remove all the solubilized copper and

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

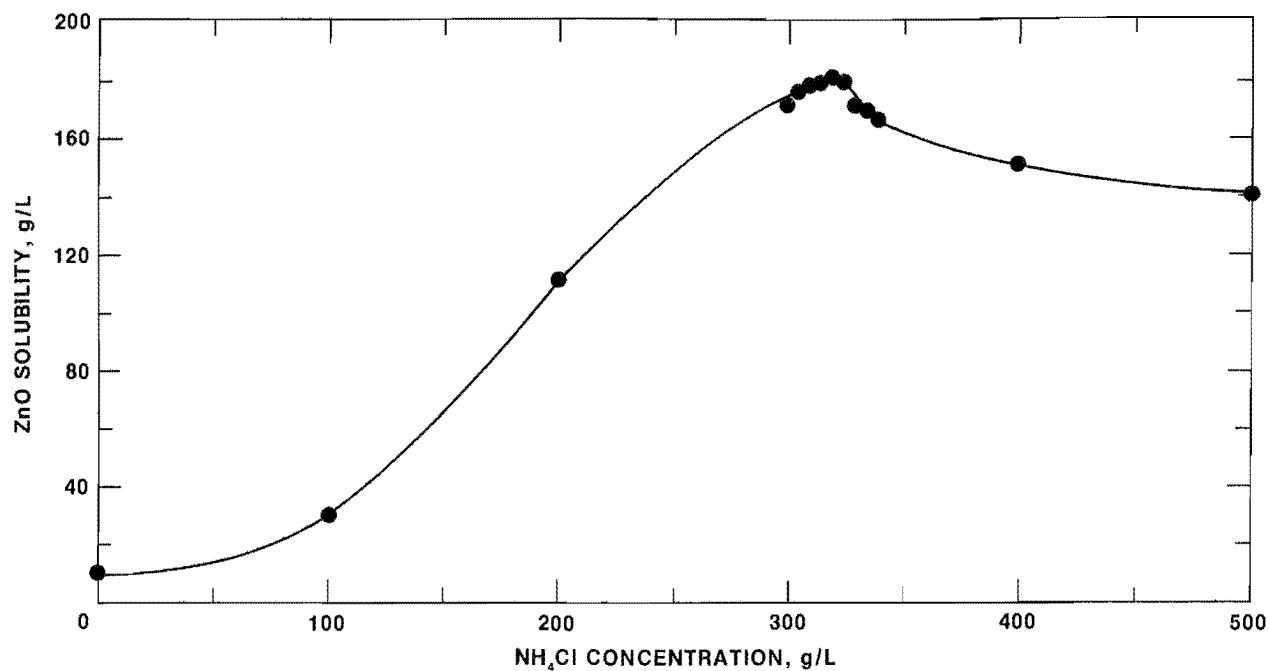


FIGURE 2. - Solubility of ZnO versus NH_4Cl content at 80°C .

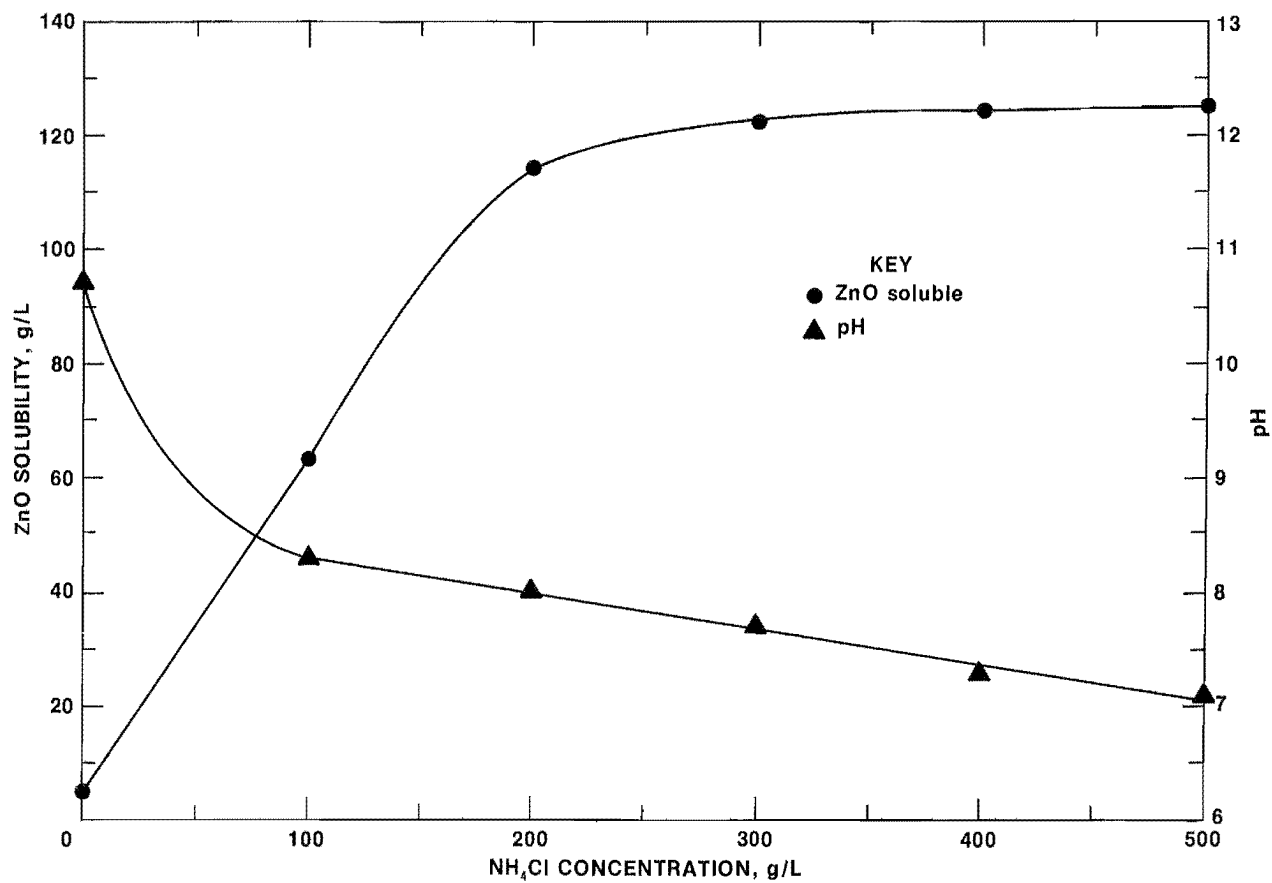


FIGURE 3. - Solubility of ZnO versus NH_4Cl content at 80°C with NH_4OH added at a level of 151 g/L.

concentration. Time and temperature tests were made using 218 g/L NH_4Cl and 70 g/L NH_4OH (sufficient to maintain a pH between 7.5 and 8.2). A 5-kg sample of converter flue dust containing 50 pct Zn, 1.0 pct Cu, 8.6 pct Pb, and 3.0 pct Sn was ground to remove lumps and then blended. From this sample, a sufficient quantity of dust was removed and split into 100-g (145 g/L) samples for the tests.

For the time study, the leach was conducted at 104° C, using a reflux condenser to minimize vapor losses. Solubility, based on the amount of residue remaining, showed that 15 min was sufficient; prolonging the leach times gave only small increases in dissolution.

To determine optimum leach temperature, leach tests were run for 15 min over the range of 75° to 104° C. Data on elements or ions leached (Zn, Cu, Pb, Cl^- , and NH_4^+) showed minimal differences over the entire range. A minimum leach temperature of 80° C was selected in order to prevent premature ZnO precipitation.

The pH range from 7.5 to 10.6 was investigated by varying the NH_4Cl concentration. The data showed that ZnO dissolution reached its practical maximum at about 200 g/L. Using these time, temperature, and NH_4Cl concentration parameters, the NH_4OH concentration was varied. The results indicated that 85 g/L NH_4OH , produced a pH of 8.2, while good solubility of ZnO was maintained. Most of the copper was also dissolved as well as some of the lead. Higher pH values were found to reduce the subsequent recovery of ZnO in the dilution step owing to its increased solubility with increasing pH. pH values of 7.5 or lower, produced by the acidic nature of the flue dust and NH_4Cl (without NH_4OH buffering), inhibit copper solubilization and, more importantly, favor the formation of zinc diammine chloride ($\text{Zn}(\text{NH}_3)_2\text{Cl}_2$) over ZnO.

Optimum leach parameters were determined to be a leach temperature of 80° C, a leach time of 15 min, and a pH of 8.2, obtained with a solution containing 200 g/L NH_4Cl and 85 g/L NH_4OH . With these

parameters, most of the copper and zinc, as well as some of the lead, is leachable from about 145 g/L flue dust.

ZINC REQUIREMENTS FOR CEMENTATION

Bench-scale tests on pregnant leach liquors produced using the above parameters required 5.0 g/L granular zinc for the ammoniacal leach solution to effectively cement copper and lead. The literature states that the amount of zinc used in cementation is usually in excess of the stoichiometric requirements (11). This is especially true where lead concentrations are high; under these conditions stoichiometric quantities of zinc metal can produce extremely fine cement particles capable of floating in the leachate. The 5 g/L Zn is near the stoichiometric requirement, and subsequent bench-scale tests confirmed that 5 g/L Zn was sufficient to cement this sample of flue dust. However, because of the wide variation of metal concentrations in converter flue dust, the process requires that an excess amount of zinc for cementation should be used to ensure complete removal of copper and lead from the pregnant leach solution.

DILUTION RATIO AND TEMPERATURE

Cement filtrates were produced using leach and cementation parameters mentioned above. The cementation filtrate contains the leached ZnO as well as the zinc metal dissolved during cementation. The ZnO is precipitated by diluting the filtrate with hot water. Precipitation of ZnO is immediate on mixing; the product was allowed to stand for 5 min to facilitate filtration. Figure 4 shows the effect of various dilution ratios (volume of water to volume of cement filtrate). For these tests, pure ZnO was dissolved in the leach solution and then precipitated by dilution above 80° C. The data in figure 4 show that maximum precipitation occurs at a dilution ratio of 3.5.

Precipitation by dilution is complicated by coprecipitation of zinc diammine

chloride ($\text{Zn}(\text{NH}_3)_2\text{Cl}_2$) at lower temperatures. X-ray diffraction data on ZnO precipitated from a typical leach solution at temperatures from 30° to 100° C showed that zinc diammine chloride was present at temperatures up to 73° C. The product is contaminated with Cl^- and NH_3

and uses up significant amounts of leach reagent. To avoid the formation of the diammine chloride, precipitations should be made at ~80° C. Higher temperatures result in greater ZnO losses due to increased solubility with temperature. (See figure 5.)

PROCESS TESTS

FLUE DUST

For the tests on the overall procedure, a new sample of converter flue dust was obtained from a major secondary copper smelter. Converter flue dust from this secondary copper smelter is recovered by two collectors in series. The dust from the primary collector has a ready market due to its high tin content (>8 pct) and was not used in this study. The dust sample for these studies was collected in fabric-celled baghouses, as is typical of the smelter's normal operations. Table 1 gives some chemical and physical properties, table 2 its chemical composition, and table 3 the trace element composition of the copper converter flue dust.

TABLE 1. - Chemical and physical properties of copper converter flue dust

Acid soluble (aqua regia).....pct..	86
Water soluble, pct:	
At room temperature...	3.5
At 100° C.....	4.4
Magnetic.....pct..	3.4
Particle size, μm :	
Average.....	<5
Largest.....	>15
Bulk density, lb/ft ³ :	
Loose pack.....	53
Dense pack.....	70
Phases present:	
Major.....	Zincite.
Minor.....	Anglesite, zinc stannate.

The flue dust was subjected to the current U.S. Environmental Protection Agency (EPA) extraction procedure for toxicity (12). Based on the results listed in table 4, the sample exceeded the

acceptable limits for lead and cadmium and would therefore be classified as a hazardous waste.

TABLE 2. - Composition of copper converter flue dust, weight percent

Ca.....	0.1	NH_4^+	0.13
Cl^-05	Pb.....	8.4
Cu.....	1.1	Sn.....	4.0
Fe.....	.16	SO_4^{--}	9.3
K.....	.09	Zn.....	60
Na.....	.09		

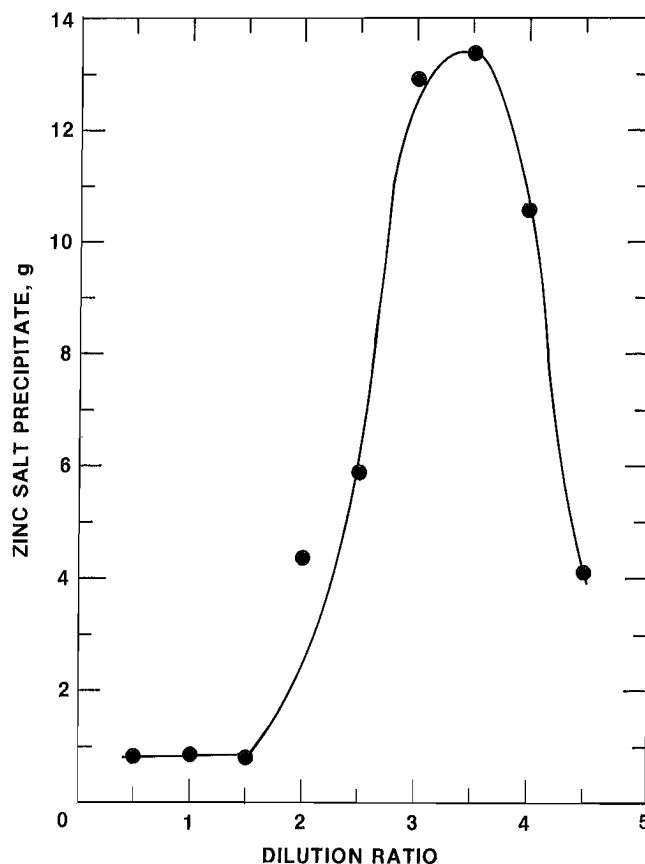


FIGURE 4. - Zinc salt precipitate versus dilution ratio.

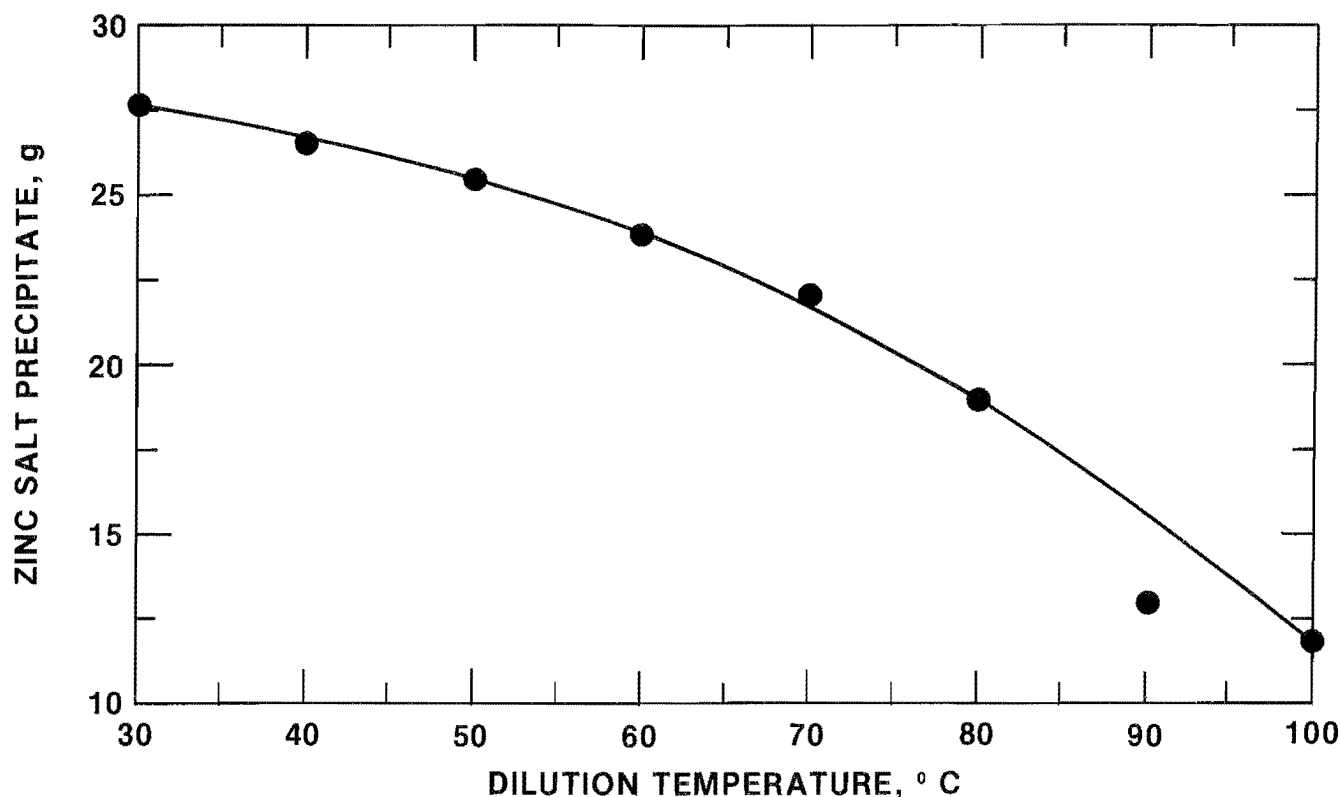


FIGURE 5. - Zinc salt precipitate versus dilution temperature.

TABLE 3. - Trace elements in copper converter flue dust¹, weight percent

Ag...	0.003 - 0.03	K....	0.03 - 0.3
Al...	.003 - .03	Li...	.0003 - .003
As...	.01 - .1	Mg...	.01 - .1
B....	.01 - .1	Mn...	.01 - .1
Bi...	.01 - .1	Mo...	.003 - .03
Cd...	.001 - .01	Na...	.03 - .3
Cr...	.003 - .03	Ni...	.003 - .03
Fe...	.03 - .3	Sb...	.003 - .03
Ga...	.03 - .3	Si...	.01 - .1
Ge...	.01 - .1	Ti...	.001 - .01
In...	.001 - .01		

¹Semiquantitative spectrochemical analysis.

NOTE.--The following elements were not detected: Ba, Co, Cs, Hg, Nb, P, Rb, Sr, Ta, Tl, V, W, Zr.

FINAL OPTIMIZED LEACH PARAMETERS

Because the new batch of flue dust obtained for the final leach tests was different from that used for the original

TABLE 4. - Concentration of selected elements in copper converter flue dust leachate compared with EPA toxicity limits

Element	Leachate conc, mg/L	EPA limit, mg/L
Ag.....	0.11	5
As.....	.002	5
Ba.....	1.8	100
Cd.....	1.7	1.0
Cr.....	.55	5
Pb.....	44	5
Se.....	.034	1.0

parameter studies, a new set of optimum parameters was determined. Leach time and temperature, cementation zinc requirements, dilution ratio, and dilution temperature were the same as for the previously studied flue dust. Maximum recovery of copper in the cement product and of ZnO required slight changes in the NH_4Cl and NH_4OH concentrations to 230 g/L and 71 g/L, respectively, with this new dust sample.

LEACH TESTS

The flowsheet for the process is shown in figure 1. The procedure consists of leaching with a hot NH_4Cl - NH_4OH solution followed by removal of the leach residue by filtration. (The leach is started at 95°C so that it does not cool below 80°C during filtration.) The pregnant leach solution is treated with granular zinc to remove copper and lead as a cement product. After removal of the cement product, the filtrate is diluted with hot water to precipitate ZnO , which is removed by filtration. The final filtrate can be recycled after being concentrated to nearly its original composition by a combination of reverse osmosis (RO) and thermal evaporation. Recent tests have shown that reverse osmosis can concentrate the filtrate to one-half its original volume, leaving about one-fourth the water for thermal evaporation. Reagent recycle was not included in the leach

tests. The specific parameters for the process are listed in table 5.

Leach tests were run to evaluate the effectiveness of each step in the process. During leaching and cementation stirring was provided with a stainless steel propeller stirrer. For sampling purposes, 10 mL of liquid were withdrawn during each step to determine the concentrations of metals.

TABLE 5. - Optimum operational parameters

Leach solution:	
Volume.....L..	1
NH_4Clg/L..	230
NH_4OHg/L..	71
Flue dust.....g..	181
Initial leach temperature..... $^\circ\text{C}$..	95
Average process temperature..... $^\circ\text{C}$..	>80
Leach time.....min..	15
Zinc metal for cementation.....g/L..	5
Dilution water ratio.....	3.5
Dilution water temperature..... $^\circ\text{C}$..	80

RESULTS

Test results confirmed that all steps of the process were operating effectively. Approximately 65 pct of the converter flue dust is soluble in the leach step, corresponding to approximately 57 pct of the copper, 4 pct of the lead, and 83 pct of the zinc. The metallic particles, PbSO_4 and Sn (present as SnO_2), are not soluble to any significant extent in this leach solution. The cementation step removes all but very low traces of

copper and lead from the leach solution. The dilution-precipitation step recovers 82 pct of the dissolved zinc. If reagent recycle is practiced, the remaining 18 pct would not be lost.

The concentration of elements of interest in the flue dust, leach residue, cement product, and the ZnO product are listed in table 6. Spectrographic analyses of minor and trace elements in the products are listed in table 7. The

TABLE 6. - Weight and composition of products from leaching copper converter flue dust with NH_4Cl - NH_4OH

Material	Weight, ¹ g	Concentration, ¹ wt pct					
		Cl^-	Cu	NH_4^+	Pb	Sn	Zn
Flue dust.....	181	0.05	1.1	0.13	8.4	4.0	60
Leach residue..	64	11	1.4	1.2	23	9.8	30
Cement product.	14	6.5	9.28	.81	16	.17	41
ZnO product....	95	3.4	$20.003-.03$.56	$20.003-.03$	ND	72

ND Not detected.

¹Dried at 110°C .

²Semiquantitative spectrochemical analyses.

TABLE 7. - Minor and trace elements in process products¹

Element	Concentration, wt pct		
	Leach residue	Cement product	ZnO product
Ag.....	0.0003-0.003	0.003 -0.03	0.0003-0.003
Al.....	.03 - .3	.01 - .1	.003 - .03
B.....	.0003- .003	.003 - .03	ND
Bi.....	.01 - .1	ND	ND
Cd.....	ND	.003 - .03	ND
Cr.....	.01 - .1	ND	ND
Fe.....	.1 - 1	.03 - .3	.003 - .03
K.....	.0003- .003	.0003- .003	.0003- .003
Mg.....	.001 - .01	.0003- .003	.003 - .03
Mn.....	.001 - .01	.0003- .003	.001 - .01
Mo.....	.01 - .1	ND	ND
Na.....	.01 - .1	.01 - .1	.01 - .1
Ni.....	.01 - .1	.003 - .03	ND
Si.....	.001 - .01	.001 - .01	.001 - .01

ND Not detected.

¹Semiquantitative spectrochemical analyses.

leach residue is salable owing to its high tin content (9.8 pct); the cement product can be recycled back to the smelter furnaces; and the ZnO product is salable as a feedstock for electrogalvanizing, or to the agricultural industry as a micronutrient additive in fertilizer and animal feed.

The ZnO produced by this process has been tested as a feedstock for electrogalvanizing wire at the Bureau's Rolla (MO) Research Center. Laboratory tests show the ZnO produces smooth coherent coatings with a finer grain structure than that obtained with pure ZnO or metal as the feedstock. The coatings are sufficiently adherent that the wire can be drawn with no breaks in the surface. The coatings have equivalent corrosion rates to those of wire electrogalvanized with either pure zinc or ZnO as feedstock.

A process evaluation has been made based on the described process together with either an evaporative system or a RO

evaporative system for recycling NH_4Cl and NH_4OH . Third-quarter 1984 prices (error margin in capital costs of ± 30 pct), a 5-st/d plant capacity, a 20-yr depreciation rate, and a rate of return of 12.2 pct were used to calculate these values. The calculations indicate that operating costs are \$0.784/lb ZnO produced for evaporation alone and \$0.585/lb for a combination of RO and evaporation. This includes credit for the tin content of the residue (\$0.266/lb) and saving for disposal (\$0.162/lb). These figures show a net return of \$0.117/lb ZnO with evaporation alone and \$0.316/lb ZnO with the RO-evaporative system. The cost for recycling the leach solution, as well as the tin content of the feed flue dust, are critical factors for this process. The use of RO cuts operating costs by \$0.20/lb ZnO, while the tin content of the feed flue dust must be in the 3.5- to 4-pct range for the present process to approach an economic balance.

SUMMARY AND CONCLUSIONS

An alkaline process to recover metal values and other products from secondary copper smelter flue dusts has been developed. The process consists of an

alkaline NH_4Cl - NH_4OH leach of the flue dust, recovery of soluble copper and lead by cementation with zinc metal, and precipitation of a ZnO product by dilution

with water. Leaching of metals from the original flue dust containing 4.0 pct Sn gave a leach residue (35 wt pct of the original flue dust) containing 9.8 wt pct Sn, which is a salable byproduct. The cement product can be recycled back to the smelter furnaces, as it is principally metallic. The ZnO product recovered has a small market in the agricultural industry as a micronutrient soil additive and additive to animal feed. Its best potential market, however, appears to be as a feedstock for electrogalvanizing. Laboratory tests at the Bureau's Rolla (MO) Research Center have shown it to be superior to pure zinc or ZnO as an electrogalvanizing feedstock.

Because all products and byproducts are either salable or potentially recyclable back to the smelter furnaces, and because the reagents can be recycled, there are only negligible quantities of environmentally nonhazardous materials for disposal.

This research illustrates that materials such as converter flue dust, which poses significant disposal or environmental problems, can be processed to recover valuable metal resources for sale or recycle with little or no material for disposal. The overall process reaches an economic balance when the tin content of the feed flue dust reaches the 3.5- to 4-pct range.

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